

trichloroborazine after a reaction period of only several hours.

Recent work in this laboratory had shown that the acetonitrile adduct of boron trichloride is a convenient reagent for synthesis of cyclic boron compounds,⁴ and our modification is based on the use of this adduct in place of gaseous boron trichloride.

Experimental Section

In a typical run 200 ml of dry chlorobenzene was placed in a 1-l. three-neck flask fitted with an inlet for dry nitrogen as a cover gas and with a water reflux condenser topped with a drying tube. Acetonitrile, 10.2 g (0.25 mole), was added to the chlorobenzene, and boron trichloride was bubbled into the solution from a lecture tank without prior purification; the resulting mixture was thoroughly stirred with a magnetic stirrer. The insoluble acetonitrile-boron trichloride adduct precipitated as formed, and after an addition time of about 20 min, fuming above the flask neck through which the boron trichloride was being added indicated that all of the available acetonitrile had reacted to form the desired complex.

Powdered, dried ammonium chloride, 14.0 g (0.252 mole), was added, and the mixture was heated at reflux temperature for 2.5 hr, by which time practically all solids had reacted to give soluble products. The solvent was removed by vacuum distillation, and the pasty residue was sublimed at 50–60° (0.2 mm). The product obtained by sublimation was identified as B-trichloroborazine by its infrared spectrum and melting point (82–84°). The yield was 8.8 g, 57% of the theoretical maximum.

(4) H. D. Smith, Jr., M.S. Thesis, St. Louis University, 1966.

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New Syntheses of Nitrosyltetracarbonylmanganese(0) and Trinitrosylcarbonylmanganese(0)

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In order to extend our investigations on the kinetics and mechanisms of substitution reactions of $\text{CoNO}(\text{CO})_3^2$ and $\text{Fe}(\text{NO})_2(\text{CO})_2^3$ to the compounds $\text{MnNO}(\text{CO})_4$ and $\text{Mn}(\text{NO})_3\text{CO}$, it was necessary to obtain these manganese compounds fairly conveniently and in reasonable quantities. Previous methods of preparation were somewhat tedious or gave the compound in low yield. The syntheses described here are experimentally easier and give higher yields of product.

$\text{MnNO}(\text{CO})_4$.—Treichel, *et al.*,⁴ prepared this compound by the reaction of $\text{HMn}(\text{CO})_5$ with NO generated from N-methyl-N-nitroso-*p*-toluenesulfonamide. Vacuum line techniques were used to fractionate the product from the reaction mixture.

During investigations of substitution reactions of

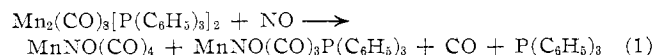
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(2) E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.*, **88**, 3929 (1966); *Inorg. Chem.*, **5**, 1691 (1966).

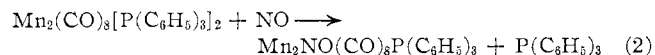
(3) D. Morris, private communication.

(4) P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 2593 (1961).

$\text{Mn}_2(\text{CO})_{10}$ it was observed⁵ that at elevated temperatures $\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$ readily reacts with CO to give $\text{Mn}_2(\text{CO})_9\text{P}(\text{C}_6\text{H}_5)_3$. Therefore, it was decided to try the same reaction using NO in place of CO. The striking result was that a *p*-xylene solution of $\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$ reacts with NO, at *ca.* 95° within seconds, almost quantitatively according to eq 1.



The mechanism of this reaction is not known, but there is some evidence in support of the reaction scheme represented by



Reaction 1 was carried out over different reaction times (10–60 sec) and with a fourfold variation in the concentration of $\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$. At all of these conditions, $\text{MnNO}(\text{CO})_4$ and $\text{MnNO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ were formed in almost equimolar amounts. This was determined by means of infrared measurements of the reaction mixtures. One would not expect such a result for an alternative mechanism that has as its initial step the formation of $\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ radicals and a subsequent substitution of $\text{P}(\text{C}_6\text{H}_5)_3$ by NO. The substitution reaction of $\text{MnNO}(\text{CO})_4$ with $\text{P}(\text{C}_6\text{H}_5)_3$ is first order in both compounds.⁶ Consequently, an equimolar formation of $\text{MnNO}(\text{CO})_4$ and $\text{MnNO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ at all of the experimental conditions appears unlikely for an Mn–Mn bond cleavage radical mechanism. Moreover, under these conditions $\text{MnNO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ is the thermodynamically stable product, and one expects a substitution of $\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ with NO as shown in (4) rather than the formation of $\text{MnNO}(\text{CO})_4$. Furthermore, $\text{MnNO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ does not react with CO (1 atm of CO in reaction flask) over a period of several days at 80°.

This reaction of $\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$ with NO allows a very convenient preparation of $\text{MnNO}(\text{CO})_4$. If tetraline is used as a solvent, $\text{MnNO}(\text{CO})_4$ can be distilled almost solvent free from the reaction solution. Further purification can be achieved by several redistillations within minutes. Usually we used *p*-xylene as a solvent. In this case, $\text{MnNO}(\text{CO})_4$ was obtained as a *p*-xylene solution, which was satisfactory for our purposes.

The yields obtained were always higher than 75%. A theoretical yield cannot be expected owing to some minor reaction of $\text{MnNO}(\text{CO})_4$ with NO or with $\text{P}(\text{C}_6\text{H}_5)_3$ that is formed by the reaction. Also at these temperatures some of the starting material is converted to $\text{Mn}_2(\text{CO})_9\text{P}(\text{C}_6\text{H}_5)_3$.⁵ Therefore, it is essential that the entire preparation procedure be finished within 5 min. Since the reaction must take place as rapidly as possible, it appears that the best starting material is $\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$. Its substitution reactions are

(5) H. Wawersik and F. Basolo, *Chem. Commun.*, 366 (1966).

(6) H. Wawersik and F. Basolo, unpublished results.

much faster than are the reactions of $\text{Mn}_2(\text{CO})_{10}$ and other $\text{Mn}_2(\text{CO})_9\text{L}$ and $\text{Mn}_2(\text{CO})_8\text{L}_2$ derivatives.⁶ This way the reaction can be stopped before $\text{MnNO}(\text{CO})_4$ reacts further with NO or L. The starting material $\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$ can be prepared photochemically by the method of Osborne and Stiddard⁷ or very conveniently by the thermal reaction described here.

$\text{Mn}(\text{NO})_3\text{CO}$.—Barracough and Lewis⁸ prepared this compound in low yield by the reaction of gaseous NO with solid $\text{Mn}(\text{CO})_5\text{I}$ or $\text{Mn}_2(\text{CO})_8\text{I}_2$.

As mentioned above, it was observed that $\text{MnNO}(\text{CO})_4$ produced in (1) reacts further with NO. This was followed up and it was found that under appropriate conditions the primary product is $\text{Mn}(\text{NO})_3\text{CO}$. Thus, a new and convenient preparation of this compound is represented by



The reaction is carried out at 90° in high-boiling solvents, from which $\text{Mn}(\text{NO})_3\text{CO}$ can be separated by distillation under vacuum. The reaction time depends on the amount of starting material used. Starting with 160 mg of $\text{MnNO}(\text{CO})_4$ we obtained $\text{Mn}(\text{NO})_3\text{CO}$ within 4 min in 50% yield. Generally the reaction with NO has to be carried out until all of the $\text{MnNO}(\text{CO})_4$ is consumed, since the two manganese compounds are difficult to separate. However, the reaction should be stopped as soon as possible, since $\text{Mn}(\text{NO})_3\text{CO}$ decomposes in the presence of excess NO. Fortunately, the infrared spectra of the two compounds differ, making it convenient to determine the extent of reaction.

Experimental Section

All of the reactions and experimental operations were carried out under nitrogen with careful exclusion of oxygen and using anhydrous solvents. The usual techniques involving Schlenk tubes and Frittes were employed. Manipulations requiring little time were done in the room light, but, for longer periods of time, light was excluded from flasks containing $\text{MnNO}(\text{CO})_4$ and $\text{Mn}(\text{NO})_3\text{CO}$. The NO was purified by successively passing it through a concentrated aqueous solution of NaOH, H_2SO_4 , KOH, and P_4O_{10} . The $\text{Mn}_2(\text{CO})_{10}$ was purchased from Alpha Inorganics.

$\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$.—In a 250-ml flask, equipped with reflux condenser and mercury bubbler, 3 g of freshly sublimed $\text{Mn}_2(\text{CO})_{10}$ and 9 g of $\text{P}(\text{C}_6\text{H}_5)_3$ in 150 ml of *p*-xylene were heated for about 15 hr at 120°. The reaction mixture, which contains $\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$, $\text{Mn}_2(\text{CO})_9\text{P}(\text{C}_6\text{H}_5)_3$, and a little unreacted $\text{Mn}_2(\text{CO})_{10}$, was cooled to room temperature and allowed to stand for several hours. During this time crystals of $\text{Mn}_2(\text{CO})_8$ -

$[\text{P}(\text{C}_6\text{H}_5)_3]_2$ separated from solution and were collected on a filter (4.2 g). The mother liquor was concentrated to ca. 50 ml and allowed to stand at room temperature in the room light for 3 days. During this time an additional 2 g of product separated from solution. The product, obtained in 95% yield, in *p*-xylene solution has an infrared spectrum in the C—O stretching region with bands at 1980 w and 1959 s cm^{-1} in agreement with the published⁷ values for $\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$.

$\text{MnNO}(\text{CO})_4$.—A suspension of finely ground $\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in 150 ml of tetraline was heated for 3 min to 95° under continuous shaking. After the compound was completely dissolved and NO was bubbled through the hot solution for 50 sec, the NO gas was turned off. A gentle stream of N_2 was passed through the solution which was also immediately cooled to room temperature using an ice bath. The reaction flask was then connected to a cold trap (−78°) using normal thick-wall Tygon tubing. The system was evacuated and allowed to distil overnight (or faster under vigorous stirring of the tetraline solution). The product was purified by several redistillations which did not take more than 2–3 min each (during the first redistillation from a mixture with some tetraline the flask should be shaken). A yield of 160–180 mg (75–83%) of $\text{MnNO}(\text{CO})_4$ was obtained which can be kept in a Schlenk tube under nitrogen and in the dark. A *p*-xylene solution of the compound has an infrared spectrum with absorption bands at 2106 w, 2034 s, 1979 s, and 1763 s cm^{-1} in agreement with the published values.⁴

Whenever tetraline in this preparation was replaced with *p*-xylene as the solvent, it distilled along with $\text{MnNO}(\text{CO})_4$. A solution of ca. 50 ml was obtained which could be used directly for the preparation of $\text{Mn}(\text{NO})_3\text{CO}$ and for other purposes.

$\text{Mn}(\text{NO})_3\text{CO}$.—A solution of 160 mg of $\text{MnNO}(\text{CO})_4$ in 40 ml of *p*-xylene was heated to 90° for 3 min. Gaseous NO was then passed through the hot solution for 4 min at which time the NO was turned off. This was replaced by a gentle stream of N_2 and the solution was immediately cooled to room temperature by means of an ice bath. The reaction mixture was passed through a fine filter and the product was distilled into a cold trap as described above. A yield of 70 mg (50%) of $\text{Mn}(\text{NO})_3\text{CO}$ in *p*-xylene solution was obtained (determined by means of infrared measurements). The compound has an infrared spectrum with bands at 2095 m, 1824 m, and 1731 s in agreement with the published values.⁸ The compound can be kept frozen in the dark and under nitrogen.

If the amount of starting materials ($\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$ or $\text{MnNO}(\text{CO})_4$) is changed in the preceding preparations, the reaction times with NO also have to be changed in order to obtain the best yields. Whenever the reaction mixture starting with $\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$ turns green, this indicates that $\text{Mn}(\text{NO})_3\text{L}$ (L = CO, $\text{P}(\text{C}_6\text{H}_5)_3$) has been formed. The reactions can be followed by taking infrared spectra of small samples from the reaction solutions in the CO or NO stretching region.

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(7) A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 634 (1964).

(8) C. G. Barracough and J. Lewis, *ibid.*, 4842 (1960).

Correspondence

Use of the Edwards Equation to Determine Hardness of Acids

Sir:

The utility of the concept of soft and hard acids and bases¹ was recently emphasized by an international

symposium held on this subject.² One limitation to the application of this concept would appear to be the difficulty of unambiguously classifying acids and bases as hard or soft. In the case of bases, a numerical order-

(1) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(2) Condensation of the symposium papers appeared in *Chem. Eng. News*, **43** 90 (May 31, 1965).